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(54) Title: CAPACITOR SUBSTRATES MADE OF REFRactory METAL NITRIDES			
(57) Abstract			
<p>Electrolytic capacitor powder substrates are provided of refractory metal nitrides to reduce instability at a substrate-oxide (as formed) interface whereby the resultant capacitor sensitivity to heat, bias and frequency is reduced.</p>			
<p>Relative Capacitance (C/C)</p> <p>Bias Voltage (V)</p> <p>● Niobium Nitride</p> <p>■ Niobium</p> <p>40V Formations</p> <p>Heat Treated 250 °C/30min</p>			

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CAPACITOR SUBSTRATES MADE OF REFRACORY METAL NITRIDES

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims priority of provisional application 60/119,010, filed 2/8/99; 10 provisional application 60/144,961, filed 7/21/99; provisional application no. 60/145,553, filed 7/23/99; provisional application no. 60/159,999, filed 10/18/99; provisional application no. 60/159,998, filed 10/18/99 and provisional application no. 60/171,835, filed 12/22/99.

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FIELD AND BACKGROUND OF THE INVENTION

The present invention relates to refractory metal nitride powders particularly those of Ta, Nb and more particularly to such powder as usable in solid electrolyte capacitors.

Solid tantalum capacitors are built on tantalum metal substrates with a dielectric layer composed of anodic tantalum oxide. A well-known problem with this structure is 20 instability caused by oxygen migration from the oxide to the metal substrate during thermal cycling (ref. 1). A gradient of oxygen deficiency with an associated conductivity profile is created across the anodic oxide film.

The present invention focuses on capacitors using a porous mass of sintered nitrides (particularly TaN, Ta₂N, NbN) as the anode and nitride powders suitable for making them. 25 The powders are referred to as "substrates" in relation to thin conversion "coatings" of dielectric oxide formed at the surfaces of the sintered powders of an anode slug (of various geometric forms) when contacted by a wet electrolyte under electro-formation conditions. In the final product the pores of the slug can be filled with a wet or solid electrolyte, but the invention is specially beneficially for solid electrolyte capacitors. Capacitors 30 containing a conductivity profile have high bias, frequency and temperature dependence of capacitance. Although capacitor manufacturers have developed procedures to minimize or eliminate the oxygen deficiency and associated conductivity profile in the dielectric, the thermodynamic instability at the metal-metal oxide interface can contribute to ignition and other failures of solid electrolyte tantalum capacitors.

35 Work over the last 30 years (ref. 2 and references therein) has demonstrated that anodic oxide films grown on tantalum substrates doped with nitrogen are more stable to

5 thermal cycling. If the nitrogen content in the tantalum exceeds 10 at, %; oxygen migration across the tantalum-tantalum oxide interface is suppressed. Capacitors made using a nitrogen doped tantalum substrate are significantly less sensitive to the effects of thermal cycling. In most cases, the substrates were thin films produced by sputtering tantalum in a nitrogen atmosphere. Sputtered substrate capacitors are found as micro
10 devices in integrated circuits. The sputtered capacitors made using a Ta₂N (33 at. % N) substrate were especially stable.

SUMMARY OF THE INVENTION

There is good potential for using TaN as the substrate for making a bilayer suitable
15 for making a solid capacitor. The anodic film grown on this substrate is insensitive to the effects of heat treatment because the presence of nitrogen blocks the migration of oxygen across the substrate-anodic film interface. The experiments show solid capacitors made of powder with the TaN anodic film system can have negligible bias, frequency and temperature dependence of capacitance and be less susceptible to failure during long term
20 aging. This was not made available to the art prior to the last 20 years (see Ref. 3 [copy appended] and references cited therein).

The use of nitrogen to improve the performance of tantalum capacitors made using tantalum as the substrate is known. U.S. patent 5,948,447, granted September 5, 1995 to H. Chang/Cabot Corp., describes nitrogen doping (at levels of 500-7000 ppm) of tantalum
25 or niobium powder substrates to reduce leakage and speculating a beneficial effect in limiting crystal growth during anodization and the benefit of higher solubility of nitrogen in tantalum or niobium (compared to oxygen) to lower leakage by limiting movement of oxygen and a synergistic effect of controlled combinations of nitrogen and oxygen content of the tantalum or niobium substrate. T. Tripp et al/H.C. Starck, Inc. in a symposium paper
30 have described a 30 year long effort to investigate the effects of nitrogen doping on tantalum substrates, mostly as to sputter deposited layers of tantalum or tantalum nitride but including also nitrogen doped powder and describe current work that verifies the effect of nitrogen in retarding migration of oxygen across the metal (Ta or Nb)-anodic oxide interface. D.J. Werder et al/Bell Telephone Labs (Thin Solid Films 323 (1998): 6-9
35 provide transmission electron microscope images showing a tantalum pentoxide anodic film formed on a sputter deposited TaN substrate with nitrogen rich inclusions in the lower

5 (toward the substrate) portion of the oxide layer that appear to be associated with a decrease of dielectric constant.

Most examples of this technique involve thin film nitrogen substrates prepared by sputtering tantalum in a nitrogen atmosphere. Niobium nitride powders are also disclosed for usage as substrates in electrolytic capacitors in the published PCT application WO 10 98/38660 (PCT/JP98/00823 filed Feb. 27, 1998 by K. Naito, Y. Uchida / Showa Denko KK), in an overall process and product system involving nitriding a niobium powder (made by chemical reduction of a niobium fluoride precursor) to produce niobium nitride powder, sintering the powder, oxidizing to form a niobium pentoxide layer (or forming such a layer in situ by a chemical vapor deposition process from an external precursor) as 15 the dielectric, incorporating a variety of electrolytes in the pores of the sintered compact but preferably organic semiconductor systems and adding a cathode and packaging to define the complete electrolytic capacitor.

The invention also includes a niobium powder that is derived directly from a pure niobium pentoxide (Nb_2O_5), e.g. by reduction of the pentoxide with a magnesium vapor to 20 form a niobium powder of extremely low oxygen impurity content and no pentoxide content at all, then introducing nitrogen in a reactor schedule that precludes re-oxidation of the niobium -- the schedule having multiple stages of thermal processing and environmental control defined below to establish a niobium nitride powder compound without excess of nitrogen remaining and eventually cooling under inert atmosphere and 25 air release of the powder to form only a limited oxide at room temperature.

Another objective is a substrate that provides for a more thermodynamically stable substrate-anodic film interface making the system less stable to the degradation that occurs in the niobium-niobium oxide system, (and even in the tantalum-tantalum oxide system) during thermal cycling.

30 Other objects, features and advantages of the invention will be apparent from the following description of preferred embodiments thereof, including illustrative non-limiting examples, of the practice of the process and the resulting products' configuration, composition and performance under test conditions.

5 FIGS. 1-9 are graphs and profiles of test results and sample conditions as described in Example 7 below.

A possible way of utilizing the ability of nitrogen to stabilize the anodic oxide films formed on Ta or Nb powders and use these to make discrete capacitors is to use a tantalum or niobium nitride (Ta₂N [33 at. %N], TaN [50 at. % N] NbN [50 at. %N]) as the substrate.
10 Those compounds can be pressed into pellets and processed using procedures similar to those in place for making solid tantalum capacitors and there is potential for making high reliability, solid capacitors with good volumetric efficiency using such nitrides.

Similar considerations apply to other refractory metal nitrides (Ti, Zr, Hf) and their uses as capacitors and other electrode forms and as catalysts, filters and for medical
15 purposes.

EXAMPLES

The invention is now further disclosed with reference to the following non-limiting Examples.

Example 1

20 **1A. Experimental Methods**

Tantalum nitride was prepared by heating 2.3 Kg of tantalum powder in three temperature stages of 700 deg., 850 deg. and 1000 deg. C. The nitrogen was introduced in the form of N₂ gas mixed with argon. The initial gas mixture was 20-mole % nitrogen. At each temperature, the powder was stepwise exposed to higher nitrogen gas concentrations
25 with a final exposure to pure nitrogen at 1000 deg. C for 30 minutes. The resulting black powder was crushed and screened.

The starting material was primary powder taken from a sodium reduction run. The physical and chemical properties of this powder are listed in Table I, below, along with those of the tantalum nitride produced. The nitrogen concentration of 6.43 W/W%
30 translates to a compound composition of TaN_{0.90}. (When the oxygen content is taken into account, the compound is TaN_{0.9} O_{0.1}.)

Pellets with a mass of 0.14 gm were pressed to a density of 5.5 g/cc and sintered at 1500 deg. C and 1600 deg. C for 20 minutes. The lead wire was tantalum. The pellets were anodized in 0.1 V/V% H₃PO₄ using a current density of 100 mA/gm and a hold time
35 at the formation voltage of 2 hours. The formation temperatures were 25 deg., 60 deg., 80 deg., 90 deg., 95 deg. C. Formation voltages were 16 and 50 volts.

5 The capacitance was measured using a HP 4262A LCR bridge without or with applied anodic bias. The maximum bias voltage was 9 volts for the 16 V formations and 25 V for the 50 V formations. Anodized pellets were heat treated in air at 400 deg. C for 30 minutes. Reformations were done in 0.1 V/V% H₃PO₄ held at the anodization temperatures. The reformation time was 2 hours.

10 **1B. Results and Discussion**

Table II, below, summarizes capacitance and leakage results as a function of formation voltage, formation temperature and pellet sintering temperature. Depending upon the conditions, the capacitance varied from a low of 23,000 to a high of 44,000 μ FV/gm. The D.C. leakage (DCL) was high for pellets formed at 50 volts. Pellets formed 15 to 16 volts at 90 deg. C and 95 deg. C had acceptably low leakages.

Table III, below, lists capacitances and leakages after heat treatment. With one exception, the capacitance dropped on average about 3%. This is in contrast to the behavior of the Ta-Ta₂O₅ system which undergoes a 7-12% increase in capacitance after heat treatment. The DCL was lower after the thermal cycle in most cases.

20 The heat-treated pellets anodized at 90 deg. C were reformed at the formation voltage for two hours at the formation temperature. The capacitance and leakage results after reformation are summarized in Table IV. With one exception the capacitance relative to the original or heat-treated value decreased 2-3 %. The leakages of all four sets of pellets were low and very low for the pellets sintered at 1600 deg. C and formed to 16 25 volts. Clearly, the heat treatment/reformation process had a very positive impact on the electrical quality as measured by the DCL.

Table V, below, summarizes the bias dependence of capacitance (BDC) after the various treatments. The BDC was taken as the percent change in capacitance between the without bias value and the highest bias value. Of major significance, is the lack of a BDC 30 after heat treatment. When the anodic film is grown on a tantalum substrate, there is a 5-10% bias dependence of capacitance after heat treatment at 400 deg. C. Of special interest is the fact that there was no BDC for the pellets that were reformed.

The lack of a bias dependence of capacitance after heat treatment is strong evidence that a conductive profile was not generated in the anodic film. This is expected if oxygen 35 is not extracted from the anodic film by the substrate and is consistent with the numerous earlier observations that anodic oxide films grown on nitrogen doped substrates are

5 resistant to oxygen migration across the metal-metal oxide interface (ref. 2). The ability of the TaN substrate to support a dielectric film that is resistant to the degrading effects of heat treatment can have a significant impact on the performance of solid capacitors made from this bi-layer system. The devices will have a low bias, frequency, and temperature dependence of capacitance and probably be more stable during accelerated life testing.

10 This latter prediction is based on the fact that life test failures are known to occur because of dielectric breakdown associated with oxygen migration within and through the anodic oxide film. The more stable oxygen environment in anodic films grown on the TaN substrate will make the system less susceptible to the long term degradation mechanisms like ignition failures associated with oxygen migration.

15 **References**

1. Smyth, D. M. Shirn, G. A., and Tripp, T. B, J. Electrochem. Soc., 110, 1264-71(1963).
2. Tripp, T. B., Shaw, M. D., and Cox, B, "The Effects of Nitrogen on the Properties of Anodic Oxide Films in Tantalum," Proceedings of CARTS 99, in press.
- 20 3. Werder, D.J., Kola, R.R. "Microstructure of Ta_2O_5 Films Grown by the Anodization of TaN_x ," 323 Thin Solid Films 6-9 (1998).

Example 2

25 Six pounds of experimental tantalum powder prepared by the reduction of K_2TaF_7 by Na in known manner,¹ was presintered at 1320°C for 30 minutes and deoxidized at 1000°C for two hours using 2 percent magnesium, in a known manner.²

Two pounds of such Ta powder were blended with 0.75% Mg and placed in a tantalum foil lined stainless steel boat. The powder was deoxidized at 950°C for two hours. The deoxidation was carried out to remove any oxygen associated with the tantalum that could interfere with a subsequent nitriding process.

30 The boat containing such mixture was placed under a slightly greater than atmospheric argon pressure, and allowed to cool overnight. Next, the boat containing such mixture was heated to 680°C as measured by a thermocouple suspended inside the furnace tube over the boat. The pressure was reduced to 600 mm Hg and nitrogen was introduced until the pressure was 760 mm Hg. The temperature was gradually increased and the

¹ See, e.g., USP 2,950,185, Hellier et al., 1960.

² See, e.g., USP 4,537,641, Albrecht et al., 1985

5 pressure was maintained between 710 and 760 mm Hg by adding nitrogen as it was consumed by reaction with the tantalum. When the temperature reached 720°C, the pressure was reduced to 460 mm Hg and the system backfilled with nitrogen to 760 mm Hg. The temperature was increased gradually to 760°C and the pressure maintained in the range of 710-760 mm Hg by adding nitrogen. The reaction was gentle as indicated by the
10 slow rate of pressure drop. At this point, the pressure was reduced to 250 mm Hg and backfilled with nitrogen to 760 mm Hg. The reaction rate increased but still remained well controlled. The temperature was allowed to increase to 830°C and the pressure was maintained at 710-760 mm Hg. Finally, the pressure was reduced to 0 mm Hg and the system back filled with nitrogen to 810 mm Hg with nitrogen. The temperature was
15 increased to give an inside temperature of 980°C and the environment was maintained at this temperature and under a slight positive pressure of nitrogen for six hours.

After cooling to room temperature, the powder was passivated. The residual magnesium oxide and Mg₃N₂ were removed by leaching with dilute H₂SO₄ followed by rinsing to remove residual acid. The leached powder was dried at 60°C.

20 The powder was analyzed for nitrogen and oxygen. The nitrogen concentration was 38,600 ppm; this corresponds to the compound Ta₂N. The oxygen concentration was 1650 ppm. The powder was tested for electrical properties before and after heat treatment and after reformation following heat treatment. The heat treatment conditions were 400°C for 30 minutes in air. The pellets were reformed at the formation voltage for 30 minutes.
25 The pellet preparation, formation and testing conditions are summarized in Table VI, below. Four pellet sets corresponding to the three sintering temperatures were formed together for each combination of formation voltage and formation temperature. In general, the anodization process went smoothly under all conditions of sintering temperature, formation voltage and formation temperature.

30 Several four-volt, 225 µF solid capacitors were made using process condition for 30-50,000 CV/gm tantalum capacitors. The powder was pressed at 4.5 gm/cm³ and sintered at 1600°C for twenty minutes. The pellet mass was 0.14 gm. No difficulties were encountered in processing. None of the finished capacitors failed. The accelerated aging was carried out at 85°C for 240 hours with an applied voltage of 6.1V. All of the
35 capacitors survived the life testing.

5 The four pellet averaged capacitance values as a function of sintering temperature, formation voltage and formation temperature after formation, after heat treatment and after reformation are summarized in Table VII, below. The capacitance ranged from a high of 38,000 CV/gm at the 1400°/60°/16V condition to a low of 18,500 CV/gm at the 1600°/90°/80V condition. The capacitance dropped from 2 to 7 percent after heat
10 treatment depending upon the formation voltage. The capacitance drop was highest for the pellets formed to 16V. In general, the capacitance drop was higher for the pellets formed at 90°C relative to those formed at 60°C. There was little further change in capacitance after the pellets were reformed.

15 The four pellet averaged leakages are collected in Table VIII, below. They ranged from a high of about 5.72 nA/µF·V to a low of 0.36 na/µF·V after formation and 7.5 to 0.16 nA/µF·V after reformation. In general, the pellets formed at 90°C had lower leakage than those formed at 60°C. The leakage increased significantly after heat treatment but in each case returned to a value close to the after-formation value for the pellet when the pellets were anodically reformed.

20 The bias dependence of capacitance after formation, heat treatment and reformation are given in Table IX, below. The bias dependence was calculated as the percent change in capacitance with an applied bias of 50 percent of the formation voltage relative to the capacitance without bias. When the substrate is tantalum, the capacitor has a negative bias dependence of capacitance of 8-10 percent after heat treatment. In the present case (Ta₂N
25 substrate), there was no bias dependence (or at most a small positive bias dependence) of capacitance after heat treatment. This is strong evidence that a conductivity profile associated with an oxygen deficiency profile does not exist in the anodic film. This property can considerably simplify the process for making solid capacitors and should give devices that are more stable under high thermal stress conditions.

30 Table X, below summarizes the results for solid capacitance. It was possible to make very good 4 volt solid capacitors from the powder. The devices performed well during accelerated life testing.

9
TABLE VI

Summary of Pellet Preparation, Formation and Testing Conditions

Condition	Value(s)
Pellet Mass	0.14gm
Press Density	5.0g/cm ³
Sintering Temperature	1400°, 1500°, 1600°C
Sintering Time	20 minutes
Formation Temperature	60°C, 90°C
Formation Voltage	16, 40, 80V
Formation Current	100mA/gm
Hold Time	2 hours
Formation Electrolyte	0.1V/V% H ₃ PO ₄
DCL Test Voltage	70%V _f
DCLL Soak Time	5 minutes
Maximum Bias Voltage	50% V _f

TABLE VII
Summary of Capacitance Results
(μ F·V.gram)

Sintering Temperature

Form. Voltage	1400		1500		1600	
	AF	AHT	AR	AF	AHT	AR
60°C Formation						

10

16	38,000	35,700	35,500	35,000	32,900	33,300	27,300	25,500	25,400
40	34,700	33,500	36,300	31,700	30,700	33,600	25,800	24,900	27,000
80	27,900	27,400	27,200	26,400	25,600	25,500	21,500	21,500	21,400

5

90°C Formation

16	34,200	31,300	23,200	31,700	29,300	32,600	25,000	23,300	24,400
40	32,200	30,000	22,500	29,200	28,300	25,300	23,300	22,600	22,600
80	34,600	30,200	22,500	19,900	19,800	20,100	18,900	18,600	18,500

*AF = After Formation

AHT = After Heat Treatment

AR = After Reformation

10

TABLE VIII

Summary of Leakage Results

(nA/μF·V)

Sintering Temperature

Form. Voltage	1400		1500			1600			
	AF	AHT	AR	AF	AHT	AR	AF	AHT	AR

15

60°C Formation

16	0.92	10.71	0.57	0.83	4.02	0.73	0.36	1.02	0.47
40	2.91	2.33	1.48	2.94	2.37	2.77	0.76	1.82	1.59
80	2.76	4.44	3.41	3.63	9.20	7.50	2.71	8.61	6.10

90°C Formation

16	0.57	3.05	0.27	0.36	1.23	0.24	0.13	0.73	0.16
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40	0.75	1.55	0.38	1.44	2.97	0.63	0.47	2.09	0.43
80	2.21	4.69	0.77	5.72	11.37	1.83	3.49	9.93	1.09

5

*AF = After Formation

AHT = After Heat Treatment

AR = After Reformation

TABLE IX

Summary of Bias Dependence of Capacitance Results

10

(Percent)

Sintering Temperature

Form. Voltage	1400			1500			1600		
	AF	AHT	AR	AF	AHT	AR	AF	AHT	AR

60°C Formation

16	-0.71	4.70	3.29	0.54	2.60	4.02	-1.01	1.71	1.10
40	0.79	0.00	-0.34	0.57	-0.05	-0.41	-0.43	0.01	-0.83
80	0.78	1.09	0.97	0.88	1.25	0.87	0.28	1.03	0.83

90°C Formation

16	-1.22	4.01	2.47	-0.60	3.90	3.79	2.47	3.79	1.54
40	0.38	-0.10	1.260	0.36	-0.40	1.41	-0.42	-0.02	0.94
80	-0.66	1.57	1.34	-0.57	0.70	0.78	-0.57	1.24	0.98

15

*AF = After Formation

AHT = After Heat Treatment

5 AR = After Reformation

TABLE X

Summary of Solid Capacitor Results

Wet DCL	Wet Cap (na/μF·V)	Solid DCL μF·V/gram	Solid Cap (na/μF·V)	Cap Rec	Yield
0.205	26,200	0.310	22,310	85%	100%

Life Test DCL (nA/μF·V)

10 **0 Hours @ 6.1V** **240 hours @ 6.1V** **Yield** **# Shorts**

25° 85° 85°C 25°C

0.310	2.249	2.105	0.279	100%	0
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Example 3

Niobium powder was made by reducing Nb_2O_5 with magnesium. The resulting powder's properties are summarized in Table XI.

15

TABLE XI

	<u>Property</u>	<u>Value</u>
	Fisher Avg. Part. Diam., FAPD (μ)	1.4
	Scott Bulk Dens., SBD (g/in ³)	16.2
	Surface Area (cm ² /g)	2.3
20	Carbon	154
	Chromium	34
	Iron	47
	Nickel	74
	Nitrogen	2880
25	Oxygen	9900
	Silicon	30
	Sulfur	13

5 One kilogram of the powder was blended with 22 gm of magnesium and placed in a niobium foil lined stainless steel tray. The tray and its contents were put in a laboratory tube furnace. The tube was flushed with argon. The temperature of the furnace was raised to 950°C and the system maintained at this temperature for 2 hours under an argon atmosphere to deoxidize the powder. The furnace was allowed to cool overnight while

10 maintaining a slight argon flow through the tube. Next, the temperature was increased to 680°C as measured with a thermocouple inside the tube suspended over the sample and the pressure was reduced to 610 mm Hg. Using nitrogen, the pressure was increased to 760 mm Hg. Over the next thirty minutes, the temperature was increased to approximately 750° and the pressure was maintained between 660 and 760 mm Hg by adding nitrogen gas

15 to replace the nitrogen consumed in the reactor. At this point, the pressure was reduced to 460 mm Hg and then increased to 760 mm Hg using nitrogen. A significant increase in the reaction rate occurred as indicated by the rate of pressure drop and an increase in the temperature. One hour after the start of the process, the temperature had reached 900°C and the reaction was proceeding at a moderate rate as indicated by the rate of pressure

20 decrease. The pressure was reduced to 250 mm Hg and then the system was returned to 760 mm Hg with nitrogen. A rapid pressure drop followed and a temperature increase occurred. The pressure was maintained at 760 mm Hg using nitrogen additions for the next 15 minutes as the temperature increased to 960°C. Following complete evacuation of the tube, nitrogen was added to bring the pressure to 760 mm Hg. Very little pressure drop

25 followed indicating the reaction was essentially complete. Finally, the pressure was increased to 810 mm Hg and the system was maintained at 1000° for six hours.

After cooling to room temperature, the powder was passivated by controlled exposure to aid. The powder was then leached with dilute sulfuric acid to remove MgO, Mg₂N₃ and residual Mg, and then with high purity water to remove traces of acid. The

30 oxygen and nitrogen content of the powder were measured using a LECO 436-oxygen/nitrogen analyzer. The nitrogen concentration was 151,000 ppm corresponding to the compound NbN without excess nitrogen. The oxygen content was 4300 ppm.

The powder was fabricated to anodes, anodized and tested in a wet electrolyte for electrical properties before and after heat treatment and after reformation at the formation

35 voltage for 30 minutes. The pellet preparation, formation, and testing conditions are summarized in Table XII.

TABLE XII

	<u>Condition</u>	<u>Value(s)</u>
10	Pellet Mass	0.14 gm
	Press Density 3.5 g/cm ³	
	Sintering Temperature(s)	1500°, 1600°, 1700°C
	Sintering Time	20 minutes
15	Formation Temperature(s)	60°C, 90°C
	Formation Voltage(s) V _f	16, 40
	Formation Current	100 mA/gm
	Hold Time	2 hours
20	Formation Electrolyte	0.1V/V% H ₃ PO ₄
	DCL Test Voltage	70% V _f
	DCL Soak Time	5 minutes
	Maxim. Bias Voltage	50% V _f

The pellets were heat-treated in air for 30 minutes at 400°C. Four pellet sets corresponding to the three sintering temperatures were formed together for each combination of formation voltage and formation temperature. It was not possible to anodize pellets sintered at 1400°C and pellets could not be anodized to 80 volts at any of the sintering temperatures

The four pellet averaged capacitance values (in $\mu\text{F}\cdot\text{V}/\text{gram}$) as a function of pellet sintering temperature, formation voltage and formation temperature, after the steps of formation (AF), heat treatment (AHT) and reformation (AR) are given in Table XIII.

TABLE XIII

Form'n Voltage	Sintering Temperature (°C)								
	1500			1600			1700		
	AF	AHT	AR	AF	AHT	AR	AF	AHT	AR
60°Formation									
16	41,000	38,600	37,900	37,700	35,800	35,400	26,400	25,000	24,700
40	40,900	40,700	38,600	37,400	36,300	35,800	26,800	26,700	25,600
90° Formation									
16	37,000	32,100	30,300	34,400	30,400	29,200	24,800	21,000	19,300
40	41,700	35,900	36,800	39,400	32,900	33,200	28,000	24,400	24,100

The capacitance ranged from a low 19,300 $\mu\text{F}\cdot\text{V}/\text{gm}$ at the 1700°/90°/16V condition and a high 41,700 $\mu\text{F}\cdot\text{V}/\text{gm}$ at the 1500°/90°/40V condition. There was an increase in capacitance when the formation voltage was increased from 16 to 40V. A similar behavior occurs with niobium when the anodization voltage increases. This is contrary to the behavior of anodes made with Ta substrates where capacitance decreases as the formation

5 voltage increases. The capacitance decreased from 0.5 to 16% after heat treatment depending upon the formation voltage and formation temperature. The capacitance change was higher for the pellets anodized at 90°C.

The leakage results (in nA/µF·V) are summarized in Table XIV.

10

TABLE XIV

Form'n Voltage	Sintering Temperature (°C)								
	1500			1600			1700		
	AF	AHT	AR	AF	AHT	AR	AF	AHT	AR
60° Formation									
16	0.60	1.31	0.58	0.29	0.50	0.26	0.24	0.65	0.27
40	0.20	1.06	0.25	0.12	0.77	0.14	0.08	0.36	0.12
90° Formation									
16	0.93	2.75	0.93	0.46	1.06	0.50	0.59	0.63	0.22
40	0.27	1.75	0.42	0.09	0.57	0.09	0.07	0.48	0.12

The highest leakage after formation was 0.60 nA/µF·V and the lowest was 0.09 nA/µF·V. In general, the heat treatment/reformation process lowered the leakage. Overall, pellets 15 with the lowest leakages were anodized at 60°C to 40 volts.

Table XV, below, shows (as a %) the bias dependence of capacitance as a function of sintering temperature, formation voltage, and formation temperature.

TABLE XV

Form. Voltage	Sintering Temperature (°C)								
	1500			1600			1700		
	AF	AHT	AR	AF	AHT	AR	AF	AHT	AR
60° Formation									
16	-0.96	-0.11	-0.20	-1.07	-0.14	-0.20	-2.06	-0.44	-0.22
40	-2.34	-0.11	-0.28	-3.37	-0.10	-0.25	-8.61	-0.41	-0.31
90° Formation									
16	-6.80	-4.56	-0.28	-6.43	-1.79	-0.17	-5.42	-3.52	-0.35
40	-14.0	-2.70	-6.03	-16.3	-0.76	-4.11	-15.2	-0.79	-3.15

20

The after formation pellets had a relatively large bias dependence of capacitance at the 90°/40V condition. This bias dependence occurs with the application of a small (~1.5V) bias and little additional bias dependence occurs as the applied bias increases. This is similar to the behavior for anodized niobium. In general, the bias dependence of 25 capacitance was low after the pellets were heat-treated. Interestingly, the high bias dependence after anodization disappears after heat treatment. The insensitivity of the system to heat treatment is striking given the fact that the anodic oxide film on niobium is severely damaged when exposed to temperatures in the 170°C range. The lack of a bias

5 dependence of capacitance after heat treatment is consistent with a model that the niobium nitride / anodic oxide film interface is more stable than the niobium metal / anodic oxide film interface.

The foregoing example with included discussion/analysis shows that it is possible to provide a niobium nitride powder and an anodized sintered pellet form thereof to serve 10 as an anode basis for capacitors with low D.C. leakage and comply with the necessary criteria of stability, reliability, cost, capacitance and ultimately fill the long extant gap between aluminum and tantalum and to some degree surpass tantalum systems. The new niobium nitride based system is suitable for solid capacitors.

Example 4

15 A similar series of powder preparation and capacitor steps, as in Example 3, was carried out (with the added step of solid electrolyte impregnation and conventional cathode application) to produce twenty 4-volt solid electrolyte capacitor powders each comprising a sintered porous (pores filled with manganese dioxide electrolyte made by thermal decomposition of manganese nitrate) anode of niobium nitride powders with anodic film 20 as the dielectric. The anodes were made up as pressed 3.5 gm blocks and sintered at 1700 deg. C. before oxidation (formation), impregnation and completion of capacitor processing. Tests of capacitance and leakage were conducted under wet and solid electrolyte environments, noting solid electrolyte presence capacitance as a percentage of wet electrolyte presence capacitance (capacitance recovery, Cap. Rec.). Wet and solid D.C. 25 leakage were also measured. The average of twenty 4 volt capacitors was 26,400 CV/gm wet capacitance, 24,100 dry, i.e. capacitance recovery of 91.5 % D.C. leakage was 0.24 nA/ μ F·V wet and 0.85 nA/ μ F·V solid. A 100 % yield was obtained in the processing and test of the group of twenty. The solid electrolyte samples were life tested through an aging period of 40 hours.

30 Initially (at essentially 0 time elapsed) the average of leakage was 0.85 nA/ μ F·V at 25 deg. C. and 6.63 nA/ μ F·V at 85 deg. C. After 40 hours of aging at 85 deg. C with an applied bias of 0.1 volts, the average of leakage at 85°C was 5.93 nA/ μ F·V and at 85 deg. C. the average of leakage was 0.81 nA/ μ F·V. There were no shorts, voltage breakdown, ignition or other runaway conditions among the 20 capacitors. All the 25 deg. C. items 35 were below the established threshold of the industry of 2.5 nA/ μ F·V, but high compared to TaN systems (studied separately and described in another co-pending provisional patent

5 application), those skilled in the art will recognize that the leakage level can be substantially reduced for NbN systems by further optimization of powder morphology, as well as sinter, formation and electrolyte impregnation conditions.

The results demonstrate an improved process for making niobium nitride (NbN) by removing the oxygen in the niobium feedstock by magnesium deoxidation prior to 10 nitriding. The nitride can be used as the substrate for making solid electrolyte capacitors with electrical quality comparable to that of devices made using tantalum as the substrate. The niobium nitride-anodic film interface is thermodynamically more stable than the niobium -anodic niobium oxide interface (and compares well vs. a tantalum-anodic tantalum oxide interface) as evidenced by the lack of a bias dependence of capacitance 15 after heat treatment for the niobium nitride substrate system.

Example 5

Tantalum powder was made by conventional sodium reduction of a potassium fluotantalate precursor and powder leaching and sizing. The powder was presintered at 20 1320° for 30 minutes and deoxidized using magnesium to remove the excess oxygen introduced during agglomeration. The resulting powder's properties are summarized in Table XVI.

TABLE XVI

	<u>Property</u>	<u>Value</u>
25	Fisher Avg. Part. Dia., FAPD (μ)	2.0
	Flow (Sec)	0.34
	Surface Area (cm^2/g)	13,700
	Scott Bulk Dens., SBD (gm/in^3)	25.5
30	Carbon	34
	Calcium	2
	Chromium	9
	Copper	1
	Iron	5
	Potassium	13
	Nitrogen	1,840
	Sodium	1

		18
5	Nickel	11
	Oxygen	4,130
	Sulfur	10
	Silicon	8

10 Approximately one kg of this powder was blended with 0.75 W/W% Mg and placed in the R&D tube furnace in a tantalum lined stainless steel tray. The furnace tube was evacuated, back-filled with argon and heated to 1000°C. This temperature was maintained for two hours to deoxidize the powder. The furnace was allowed to cool overnight.

15 The temperature was increased to 680°C as measured with a thermocouple inside the tube and suspended over the powder. The pressure in the tube was reduced to 610 mm Hg and the system back-filled with nitrogen until the pressure returned to atmospheric (760 mm Hg). Additional nitrogen was added to maintain an approximate atmospheric pressure as the nitrogen was consumed by reaction with the tantalum. Twenty minutes into the process, the pressure was reduced to 460 mm Hg and then increased to 20 760 mm Hg with nitrogen. At this point, the temperature was 710°C. Again, the pressure was maintained at near atmospheric with nitrogen additions as the temperature was increased over the next 25 minutes to 850°C. The pressure was reduced to 250 mm Hg and increased back to 760 mm Hg with nitrogen. While maintaining near atmospheric pressure in the tube using nitrogen additions, the temperature was increased to 1030° over a period 25 of 50 minutes. The pressure was then reduced to ~0 mm Hg and the system filled with nitrogen to 810 mm Hg. The system was maintained at this temperature and pressure for five hours.

30 The furnace was allowed to cool to room temperature and the powder was passivated using the high capacitance powder passivation cycle. The powder was leached with dilute H₂SO₄ solution to remove the MgO, Mg₂N₃ and any residual Mg. The residues of acid were removed by rinsing with high purity water. The powder was dried to 60°C.

35 The powder was analyzed for oxygen and nitrogen using a Leco 436 oxygen/nitrogen analyzer. The oxygen concentration was 2840 ppm and the nitrogen content was 6.99% W/W% (75,200 ppm). This corresponds to the compound TaN_{0.97}.

35 The powders were tested for electrical properties before and after heat treatment and after reformation following heat treatment. The heat treatment conditions were 400°C

5 for 30 minutes in air. The pellets were reformed at the formation voltage for 30 minutes. The pellet preparation, formation and testing conditions are summarized in Table XVII.

TABLE XVII

	<u>Condition</u>	<u>Value(s)</u>
10	Pellet Mass	0.14 gm
	Press Density	5.0g/cm ³
	Sintering Temperature	1500°, 1600°, 1700°C
15	Sintering Time	20 minutes
	Formation Temperature	60°C, 90°C
	Formation Voltage	16, 40, 80
	Formation Current	100 mA/gm
	Hold Time	2 hours
20	Formation Electrolyte	0.1V/V% H ₃ PO ₄
	DCL Test Voltage	70% V _f
	DCL Soak Time	5 minutes
	Maxim. Bias Voltage	50% V _f
25	Four pellet sets corresponding to the three sintering temperatures were formed together for each combination of formation voltage and formation temperature. In general, the anodization process went smoothly under all conditions of sintering temperature, formation voltage and formation temperature. The four pellet averaged capacitance values (in μ F·V/gram) as a function of pellet sintering temperature, formation voltage and formation	
30	temperature, after the steps of formation (AF), heat treatment (AHT) and reformation (AR) are given in Table XVIII.	

TABLE XVIII

Form'n Voltage	Sintering Temperature (°C)								
	1500			1600			1700		
	AF	AHT	AR	AF	AHT	AR	AF	AHT	AR
60° Formation									
16	35600	33300	32900	28300	26500	26400	18100	17000	16800
40	32600	31800	31900	26600	26300	26100	17600	17400	17400
80	26700	26900	26300	23000	22900	22500	15900	15900	15800
90° Formation									
16	32500	30800	30500	26300	24900	24700	16600	15700	15600

20

40	28100	28100	27900	24200	23800	23800	15700	15600	15700
80	20400	19300	15600	18000	17300	133300	13800	13600	13500

5

The capacitance ranged from a high of 35,600 $\mu\text{F}\cdot\text{V}/\text{gm}$ at the 16V/60°/1500° condition to a low of 13,800 $\mu\text{F}\cdot\text{V}/\text{gm}$ at the 80V/90°/1700° condition. As with Ta_2N and NbN substrate capacitors, the capacitance decreases after heat treatment and after 10 reformation.

The leakage results (in $\text{nA}/\mu\text{F}\cdot\text{V}$) are summarized in Table IXX.

TABLE IXX

Form. Voltage	Sintering Temperature (°C)								
	1500			1600			1700		
	AF	AHT	AR	AF	AHT	AR	AF	AHT	AR
60° Formation									
16	1.40	9.89	2.25	0.33	0.54	0.31	0.31	0.70	0.28
40	2.06	3.79	1.09	1.72	2.11	0.63	1.23	2.89	0.67
80	3.92	3.55	3.41	4.00	3.38	3.39	3.89	3.70	3.42
90° Formation									
16	0.39	6.17	0.42	0.16	0.36	0.12	0.18	0.55	0.16
40	0.80	1.92	0.28	0.79	1.59	0.71	0.46	1.61	0.17
80	5.72	12.87	4.84	8.15	13.47	6.21	6.07	13.73	5.07

15 The leakages increased as the formation voltage increased and the sintering temperature decreased. At the 16V and 40V formation conditions, the leakage decreased as the formation temperature increased. The reverse occurred at the 80V condition. In general, the leakages were lowest after reformation. The leakages for the TaN/anodic film 20 capacitors are higher than the ones for Ta_2N /anodic film capacitors and NbN/anodic film capacitors (production and testing described in separate co-pending provisional applications) at the 16V and 40V conditions. Except at the highest formation voltages, the leakages were in most cases acceptably low.

25 Table XXV, below, shows (as a %) the bias dependence of capacitance as a function of sintering temperature, formation voltage, and formation temperature.

TABLE XXV

Form. Voltage	Sintering Temperature								
	1500			1600			1700		
	AF	AHT	AR	AF	AHT	AR	AF	AHT	AR
60° Formation									
16	-0.31	-0.05	-0.01	-0.29	-0.04	-0.09	-0.41	-0.04	-0.12
40	-0.18	-0.10	-0.07	-0.20	-0.09	-0.07	-0.19	-0.11	-0.05
80	-0.10	-0.10	-0.11	-0.12	-0.12	-0.13	-0.11	-0.10	-0.11
90° Formation									
16	-0.32	-0.05	-0.02	-0.32	0.00	0.08	-0.38	-0.08	0.09
40	-0.16	-0.08	-0.08	-0.19	-0.08	-0.09	-0.15	-0.08	-0.07
80	-0.10	-0.11	-0.06	-0.10	-0.11	-0.07	-0.10	-0.06	-0.05

It is seen that the tantalum nitride/anodic film system is very insensitive to heat treatment.

10 TaN is better than Ta₂N and NbN in resisting the effects of heat treatment.

The foregoing example with included discussion/analysis shows that it is possible to provide a tantalum nitride powder and an anodized sintered pellet form thereof to serve as an anode basis for capacitors with low D.C. leakage and comply with the necessary criteria of stability, reliability, cost, and capacitance. The system is suitable for solid

15 capacitors.

Example 6

A similar series of powder preparation and capacitor steps, as in Example 1, was carried out (with the added step of solid electrolyte impregnation and conventional cathode application) to produce twenty 4-volt solid electrolyte capacitor powders each comprising

20 a sintered porous (pores filled with manganese dioxide electrolyte made by thermal decomposition of manganese nitrate) anode of niobium nitride powders with niobium pentoxide as the dielectric. The anodes were made up as pressed 5.5 gm. blocks and sintered at 1600 deg. C. before oxidation (formation), impregnation and completion of capacitor processing. Tests of capacitance and leakage were conducted under wet and

25 solid electrolyte environments, noting solid electrolyte presence capacitance as a percentage of wet electrolyte presence capacitance (capacitance recovery, Cap. Rec.). Wet and solid D.C. leakage were also measured. The average of twenty 4-volt capacitors was 27,500 CV/gm wet capacitance, 24,600 dry, i.e. capacitance recovery of 89.6 %. D.C.

leakage was 0.26 nA/μF·V wet and 0.14 nA/μF·V solid. A 100 % yield was obtained in

30 the processing and test of the group of twenty. The solid electrolyte samples were life tested through an aging period of 40 hours.

5 Initially (at essentially 0 time elapsed) the average of leakage was 0.14 nA/ μ F·V at 25 deg. C. and 1.29 nA/ μ F·V at 85 deg. C. After 40 hours of aging at 85 deg. C with an applied bias of 6.1V, the average of leakage was 1.44 nA/ μ F·V and at 25 deg. C. the average of leakage was 0.18 nA/ μ F·V. There were no shorts, voltage breakdown, ignition or other runaway conditions among the 40 capacitors. All the. items were below the 10 established threshold of the industry of 2.5 nA/ μ F·V.

The results demonstrate an improved process for making tantalum nitride (TaN) by removing the oxygen in the tantalum feedstock by magnesium deoxidation prior to nitriding. The tantalum nitride can be used as the substrate for making solid electrolyte capacitors with electrical quality comparable to that of devices made using tantalum as the 15 substrate. The tantalum nitride-anodic tantalum oxide film interface is thermodynamically more stable than the tantalum-anodic tantalum oxide interface as evidenced by the lack of a bias dependence of capacitance after heat treatment for the tantalum nitride substrate system.

Example 7

20 The appended published paper (Tripp, Creasi and Cox "Tantalum Nitride: A New Substrate For Solid Electrolyte Capacitors"), including all its text, footnotes (and the publications and presentations defined thereby) and drawings is incorporated herein by reference as though set out at length herein. The disclosure overlaps in part with the preceding Examples but also includes additional information.

TANTALUM NITRIDE: A NEW SUBSTRATE FOR SOLID ELECTROLYTE CAPACITORS

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ABSTRACT

Tantalum has been the metal of choice as a substrate for solid electrolyte capacitors since their invention in the late 1950's. This is so in large part because of the excellent insulating properties of the anodic oxide film that serves as the capacitor dielectric. It is well known, however, that because of the inherent thermodynamic instability at the tantalum anodic tantalum oxide interface, solid tantalum capacitors are adversely affected by exposure to high temperatures during manufacturing and use. At elevated temperatures, the tantalum extracts oxygen from the adjacent anodic oxide leaving oxygen vacancies in the dielectric. As a result of the conductivity associated with this oxygen deficiency, tantalum substrate solid capacitors will have high bias, temperature and frequency dependencies of capacitance if not treated to repair the damage generated by exposure to high temperature; for example, during the pyrolysis of manganese nitrate. This adds to the complexity and cost of capacitor manufacture. A way to eliminate the problems associated with the tantalum - anodic tantalum oxide system is to use a substance that reduces the thermodynamic instability at the substrate - anodic film interface. A compound that fulfills this requirement and is suitable as a substrate for solid capacitors is tantalum nitride. Capacitors based on this material are insensitive to the effects of heat treatment and solid capacitors perform well during accelerated life test.

INTRODUCTION

It is well known that capacitors based on the tantalum - anodic tantalum oxide film system are susceptible to dielectric degradation when exposed to temperatures in excess of 200 °C¹⁻³. The tantalum substrate extracts oxygen from the anodic oxide leaving a gradient of oxygen vacancies and associated conductivity across the dielectric. A heat treated

tantalum capacitor will have high bias, temperature and frequency dependencies of capacitance and elevated ESR if it is not processed to eliminate the oxygen deficiency and conductivity profile. This treatment adds significantly to the complexity and cost of manufacturing solid tantalum capacitors. Furthermore, the capacitor is still susceptible to the effects of heat treatment, for example, during the reflow soldering process and extended operation at elevated temperatures.

Recently, we reported that even 2000 ppm nitrogen stabilizes the tantalum - anodic tantalum oxide system against oxygen migration during heat treatment⁵. Capacitors made from nitrogen doped tantalum had a smaller bias dependence of capacitance after heat treatment than capacitors made from undoped tantalum. Beginning in the 1970's, a number of studies of anodic films on sputtered TaN_x substrates⁶⁻¹⁰, demonstrated that this system is stable when exposed to elevated temperatures. These results suggest that capacitors made from tantalum nitride powder should be insensitive to high temperature exposure and thermal cycling. This model was confirmed by our recent investigation of the suitability of tantalum nitride powder as a substrate for solid capacitors.

EXPERIMENTAL

The tantalum nitride was prepared by reacting capacitor grade tantalum powder with nitrogen gas using a proprietary process. No attempt was made to optimize the physical properties of the powder for use in automated pellet presses. The powder was analyzed for oxygen and nitrogen using a Leco TC-436 Oxygen:Nitrogen Analyzer. The sample weight was adjusted to compensate for the high nitrogen concentration compared to the level encountered in capacitor grade tantalum powders.

Anodic film chemical composition depth profiles were measured by Scanning Auger Microanalysis (SAM) using a Perkin Elmer Model 600 Auger Spectrometer. The sputtering rate was approximately 200 Å/min on a sample area of 100 X 100 microns using 3 KV argon ions.

Capacitors were made from 0.14 gm pellets pressed at a density of 5.5 gm/cc; the lead wire was tantalum. The sintering time was 20 minutes. The formation conditions were typical of those used for the anodization of tantalum and are summarized in Table

Table 1 Formation Conditions

Formation Electrolyte	0.1 V/V% H3PO4
Formation Temperature	60 °C, 90 °C
Formation Voltages	16V, 40V, 80V
Current Density	100 mA/gm
Hold Time	2 hours

I. Heat treatments were carried out at 400 °C for 30 minutes in air. The pellets were reanodized after heat treatment for 1 hour at the formation voltage using the same electrolyte conditions used for formation. The capacitance was measured with a Hewlett Packard Model 4274A LCR bridge operating at 120 Hz without and with an applied anodic bias equal to 50 percent of the formation voltage. The DC leakage current (DCL) was measured 5 minutes after the application of a bias voltage equal to 70 percent of the formation voltage.

Solid capacitors were fabricated by hand in lots of 20 units. The processing conditions were the same as used to make solid tantalum capacitors with comparable capacitance and voltage rating. The derating was 4X. The life testing conditions were 40 hours at 85 °C with an applied anodic bias of 1.35X the rated voltage.

RESULTS AND DISCUSSION

The nitrogen concentration in the tantalum nitride powder used in the investigation was 7.19 W/W%, based on the average of five measurements, which corresponds to the compound $TaN_{1.00}$. The oxygen concentration was 2540 ppm. The nitrogen and oxygen concentrations after heating samples of tantalum nitride in vacuum for 30 minutes at temperatures between 1100 °C and 1600 °C are plotted in Figure 1. At a temperature between 1200 °C and 1300 °C, the powder starts to lose nitrogen and at temperatures above 1400 °C, the nitrogen concentration is about 3.4 W-W% corresponding to

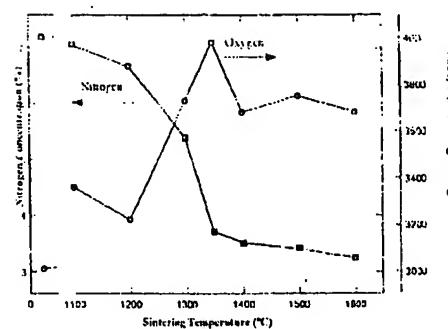


Figure 1 Pellet nitrogen and oxygen as a function of sintering temperature.

$Ta_{2.2}N$ which is close to the compound Ta_2N . The actual capacitor substrate studied in this investigation was closer to Ta_2N than TaN . The oxygen concentration increased 600-700 ppm after sintering at temperatures above 1300 °C. The oxygen concentration in tantalum typically increases 1000-1500 ppm after sintering.

The results of a SAM depth profile study of sintered and anodized sintered pellets are plotted in Figure 2. The pellets were sintered at 1600 °C for 20

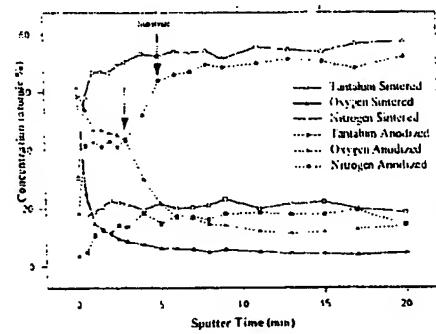


Figure 2 SAM depth profiles.

minutes. Consistent with earlier investigations using sputtered Ta_2N substrates^{11, 12}, the anodic film was composed of two layers. The outer layer, rich in oxygen, presumably was formed as a result of net tantalum migration through the anodic film and reaction at the electrolyte - film interface. The inner layer grows as a result of oxygen migration through the film and reaction with the substrate at the substrate - anodic film interface. The nitrogen concentration is

higher in this portion of the film than it is in the outer layer.

A few comments regarding the relative thickness of the layers are in order. The transport number of tantalum through the anodic film growing on a tantalum substrate is 0.24¹³ and the portion of the film produced by growth at the electrolyte interface is about 25 percent of the total film thickness. For the film grown on the tantalum nitride substrate, about 60 percent of the total film thickness was produced at the electrolyte - anodic film interface. The transport number of tantalum must be higher in an anodic film grown on the nitride substrate than it is in an anodic films grown on pure tantalum. This conclusion contradicts the reported slight decrease in the tantalum transport number as the nitrogen concentration increases¹¹ in sputtered nitrogen doped substrates, but is consistent with the evidence that nitrogen in the anodic film suppresses oxygen migration.

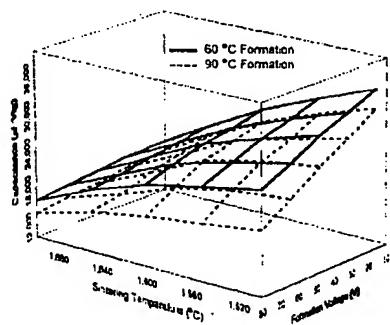


Figure 3 Capacitance as a function of sintering temperature, formation temperature and formation voltage.

The capacitance as a function of sintering temperature, formation voltage and formation temperature is summarized in Figure 3 and Table II. The dependence of the capacitance on these inputs is

Table II Summary of Capacitances (μF/V/gm) Tantalum Nitride substrate capacitors.

Formation Voltage	Formation Temperature					
	60 °C			90 °C		
	Sintering Temperature			Sintering Temperature		
	1500 °C	1600 °C	1700 °C	1500 °C	1600 °C	1700 °C
16	35,600	28,300	18,100	32,500	26,300	16,600
40	32,600	26,600	17,600	28,100	24,200	15,700
80	26,700	23,000	15,900	20,400	18,000	13,800

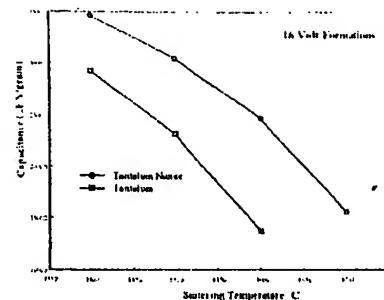


Figure 4 Capacitance as a function of sintering temperature for tantalum nitride and tantalum substrate capacitors.

comparable to that of the tantalum system. The sintering temperature dependencies of capacitance for tantalum nitride and tantalum substrate capacitors are compared in Figure 4. The tantalum powder was selected to have a capacitance in the range of the tantalum nitride substrate system. The tantalum nitride system is less sensitive than the tantalum system to changes in sintering temperature.

Table III contains results for capacitors made from tantalum nitride and tantalum substrate capacitors with the same surface area. This was achieved by sintering the tantalum nitride at 1700 °C and the tantalum at 1515 °C to give sintered 0.14 gm pellets with a surface area of 380 cm². The ratio of the tantalum nitride to tantalum substrate capacitances is about 0.6 indicating that the dielectric constant to anodic film thickness ratio for the nitride system is

Table III Summary of capacitances (μF/V/gm) for Tantalum Nitride and Tantalum substrate capacitors with the same surface area.

Powder	Formation Voltage	
	16 V	30 V
Tantalum Nitride	13,800	13,200
Tantalum	21,600	22,000

about 60 percent of this ratio value for the tantalum system. If we assume that the formation factor (A/V) for the tantalum nitride and tantalum systems is the same^{11,14}, then the dielectric constant of the anodic film on the tantalum nitride is about 60 percent of the dielectric constant of anodic tantalum oxide or around 15. This is in reasonably good agreement with the dielectric constant of the anodic film grown on a sputtered Ta₂N substrate^{11,14}.

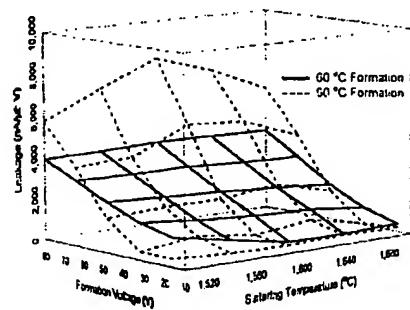


Figure 5 Leakage as a function of sintering temperature, formation temperature and formation voltage.

Figure 5 and Table IV summarize the DCL of tantalum nitride substrate capacitors as a function of

sintering temperature, formation voltage and formation temperature. At the lower formation voltages, the capacitors formed at 90 °C had lower DCL than those formed at 60 °C. The reverse occurred when the formation voltage was 80 volts.

A meaningful comparison of the leakages of tantalum nitride and tantalum substrate capacitors requires examination of units with the same surface areas. Because of the difference in the dielectric constant of tantalum nitride and tantalum substrate anodic films, it is not possible to normalize the leakages with the capacitor charge (CV). For the same surface area capacitors described above, at the 16 V formation condition, the tantalum nitride and tantalum substrate capacitor leakages are 1.29 nA/cm² and 0.56 nA/cm² respectively. The leakage of the tantalum nitride system capacitors was about twice that of the tantalum system. After the capacitors were heat treated in air for 30 minutes at 400 °C and then reformed at the formation voltage for 1 hour, the leakage for the tantalum nitride system was 0.31 nA/cm² and 0.30 nA/cm² for the tantalum system. For the pellets formed to 30 V, the tantalum nitride and tantalum substrate leakages were 1.67 nA/cm² and 0.55 nA/cm² respectively. The leakage dropped to 1.21 nA/cm² and 0.26 nA/cm² after heat treatment and reformation. In general, the leakage of tantalum nitride substrate capacitors is higher than that of tantalum substrate capacitors, but is reduced by heat

Table IV Summary of Leaks (nA/μF-V) Tantalum Nitride substrate capacitors.

Formation Voltage	Formation Temperature					
	60 °C			90 °C		
	Sintering Temperature			Sintering Temperature		
	1500 °C	1600 °C	1700 °C	1500 °C	1600 °C	1700 °C
16	1.40	0.33	0.31	0.39	0.16	0.18
40	2.06	1.72	1.23	0.80	0.79	0.46
80	3.92	4.00	3.89	5.72	8.15	6.07

Table V Summary of 6V tantalum nitride solid capacitor evaluation.

Powder	Wet and Solid Electrical Properties			
	Wet DCL (nA/μF-V)	Wet Capacitance (μF-V/cm)	Wet DCL (nA/μF-V)	Wet Capacitance (μF-V/cm)
Tantalum Nitride	0.49	24,700	0.11	23,600
Tantalum	0.07	29,000	0.07	28,800
Life Test DCL (nA/μF-V)				
0 Hrs @ 1.53 x Vr		40 hrs @ 1.53 Vr		
25 °C	85 °C	85 °C	25 °C	
Tantalum Nitride	0.11	0.99	0.81	0.10
Tantalum	0.07	0.63	0.56	0.08

treatment and reformation to the point where at low formation voltages it approaches that of anodic tantalum oxide.

Table V contains the results from the evaluation of tantalum nitride substrate, solid capacitors. Solid capacitors made from tantalum were processed concurrently and the results for this system are included. One set of tantalum anodes was sintered at the same temperature as the tantalum nitride anodes. The sintering temperature of the other set of tantalum capacitors was adjusted so that the capacitance was close to that of the tantalum nitride substrate capacitors. Notice the significant drop in the leakage of the tantalum nitride capacitors following solids processing. This is due to the heat treatment and reformation associated with the solid capacitor manufacturing process. The tantalum nitride substrate capacitors performed as well as the tantalum substrate capacitors during the accelerated life test.

The bias dependencies of capacitance of tantalum nitride and tantalum substrate capacitors, after heat treatment at 400 °C in air for 30 minutes, are compared in Figure 6. The tantalum capacitor had a

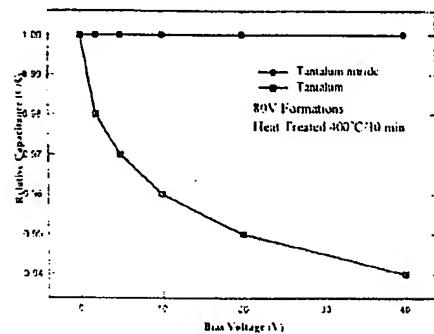


Figure 6 The bias dependence of capacitance of tantalum nitride and tantalum substrate capacitors.

significant bias dependence of capacitance while the capacitance of the tantalum nitride substrate capacitor was essentially independent of applied bias. The reason for this difference in the response of the two systems to applied bias after heat treatment can be deduced from the conductivity profile model for the effect of heat treatment on the electrical properties of anodic oxide films on tantalum.^{1,2}

When the tantalum - anodic tantalum oxide system is exposed to temperatures above about 200 °C in air, the tantalum substrate extracts oxygen from the

oxide leaving oxygen vacancies and associated n-type semiconduction because of the thermodynamic instability at the metal - oxide interface. Following heat treatment, a gradient of conductivity, σ , exists across the anodic oxide film as depicted in Figure 7.

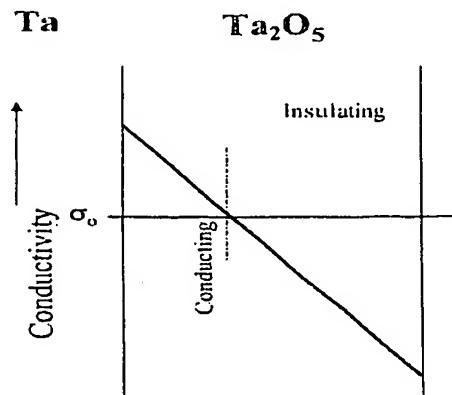


Figure 7 The conductivity profile.

The conductivity σ_0 is the value that distinguishes insulating from conducting oxide. One consequence of heat treatment is a decrease in the effective dielectric thickness, and an associated increase in capacitance. The temperature and frequency dependencies of capacitance are due to the change in effective dielectric thickness with changes in the measuring temperature and frequency as described elsewhere.^{1,2} The effect of applied anodic bias on the shape and position of the conductivity profile is shown in Figure 8. As the bias voltage is increased, electrons trapped in the oxygen vacancies are extracted into the tantalum and the thickness of the insulating layer increases as shown in Figure 8A. The result is a

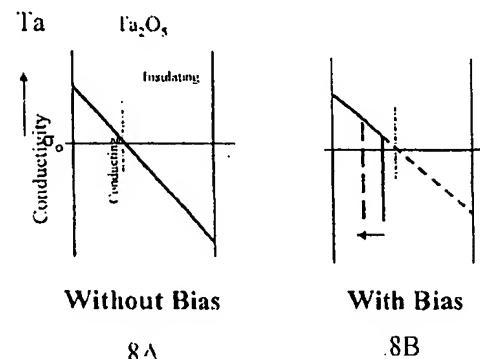


Figure 8 The effect of anodic bias on the conductivity profile.

decrease in capacitance as the bias voltage increases until the effective insulating layer reaches the full oxide thickness after which the capacitance is insensitive to further increases in applied bias as seen in Figure 8B. Measuring the bias dependence of capacitance is an easy way of determining if the heat treatment created an oxygen deficiency in the dielectric as a result of oxygen extraction from the anodic film by the substrate.

Since the tantalum nitride substrate capacitor had no bias dependence of capacitance there was no conductivity profile in the anodic film. This means that the substrate did not extract oxygen from the anodic film during heat treatment. This is consistent with the earlier results cited above and the higher thermodynamic stability of the tantalum nitride - anodic film interface relative to the one in the tantalum anodic tantalum oxide system. One proposed mechanism for how dissolved nitrogen suppresses oxygen extraction into a sputtered Ta_2N substrate is that it occupies the majority of interstitial sites in the tantalum lattice^{7,9}. Also if the tantalum nitride is a chemical compound, than oxidation of the substrate by oxygen from the anodic film requires additional energy to break the Ta-N bonds⁹. Viewed thermodynamically, the tantalum nitride is a weaker reducing agent than tantalum and consequently is less able to reduce the anodic film even when the system is exposed to high temperature for an extended period.

Figure 9 compares the bias dependencies of capacitance of niobium nitride (NbN) and Nb substrate capacitors after heat treatment in air at 250 °C for 30 minutes. The sensitivity of the niobium - anodic niobium oxide system to heat treatment is well documented¹⁰ and is a major impediment to the use of this metal as the substrate in solid capacitors. The capacitance of the heat-treated niobium nitride substrate capacitors was insensitive to applied bias providing strong evidence that this system is stable to thermal cycling. This is further evidence for the ability of nitrogen to stabilize the substrate - anodic film system to oxygen migration at elevated temperatures. Niobium nitride could be an alternative to niobium as a solid capacitor substrate.

The insensitivity of the tantalum nitride - anodic film system to heat treatment can have positive effects on solid capacitor manufacturing and the performance of capacitors made from this system. The manganization process can be carried out at high temperatures without the required post treatments needed to remove the dielectric oxygen deficiency created during the thermal cycling of tantalum substrate capacitors. Tantalum nitride substrate

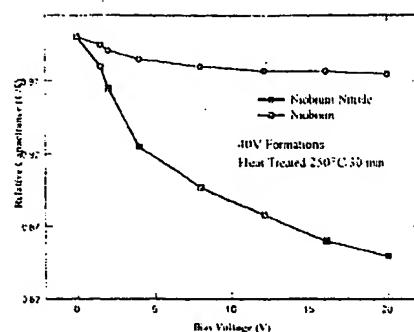


Figure 9 The bias dependence of capacitance of niobium nitride and niobium substrate capacitors.

capacitors will not degrade during the thermal cycling associated with reflow soldering. Failure mechanisms in tantalum substrate capacitors associated with oxygen migration, especially at elevated operating temperatures will be eliminated.

A serious problem with solid tantalum capacitors made from high surface area, tantalum powder is catastrophic ignition failures. One measure of the flammability of metal powders is the minimum energy required to ignite a dust cloud. This minimum ignition energy for high capacitance tantalum powders is < 3 mJ. The minimum ignition energy for the tantalum nitride powder is >10 J. It is very difficult to ignite tantalum nitride. Consequently, ignition failures will be virtually eliminated if the solid capacitor substrate is tantalum nitride.

CONCLUSIONS

Sintered pellets made from tantalum nitride powder can be anodized to give an anodic film suitable as the dielectric in a capacitor. Solid capacitors made from this system perform as well as solid capacitors made using a tantalum powder substrate. In contrast to the tantalum - anodic tantalum oxide system, the tantalum nitride - anodic film system is insensitive to the effects of heat treatment. This property can simplify the solid capacitor manufacturing process and reduce failures caused by oxygen migration during elevated temperature operation. Solid capacitors made from tantalum nitride will not undergo ignition failures because of the greatly reduced tendency of tantalum nitride relative to tantalum to react with oxygen.

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30

5 It will now be apparent to those skilled in the art that other embodiments, improvements, details, and uses can be made consistent with the letter and spirit of the foregoing disclosure and within the scope of this patent, which is limited only by the following claims, construed in accordance with the patent law, including the doctrine of equivalents.

What is claimed is:

5 1. A refractory metal nitride powder suitable as a substrate for electrolytic capacitors and comprising a refractory metal nitride powder selected from and characterized in an ability when tested or otherwise subjected to capacitor anode sintering and formation and electrolytic capacitor production and life test conditions by display of an oxide of Ta, Nb interface with the substrate powder that is substantially insensitive to

10 10 heating of such test conditions and reduced bias and frequency dependence compared to un-nitrided analogs.

2. The powder of claim 1 wherein the refractory metal nitrides are selected from the group consisting of substantially (atomic basis) TaN, Ta₂N, NbN.

3. An electrolytic capacitor anode comprising the powder of claim 2.

15 4. A wet electrolytic capacitor comprising the anode of claim 3.

5. A solid electrolyte capacitor comprising the anode of claim 3.

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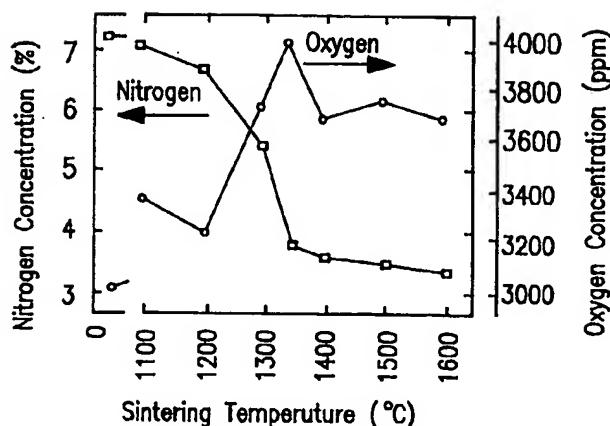


FIG. 1

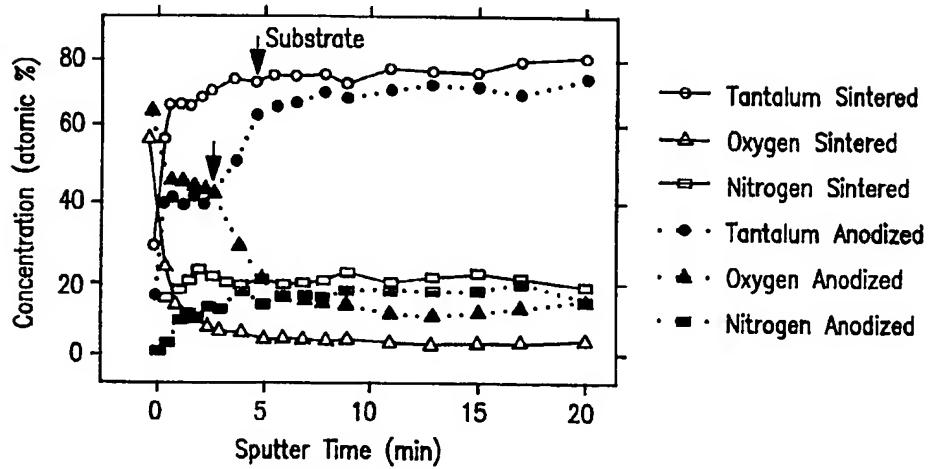


FIG. 2

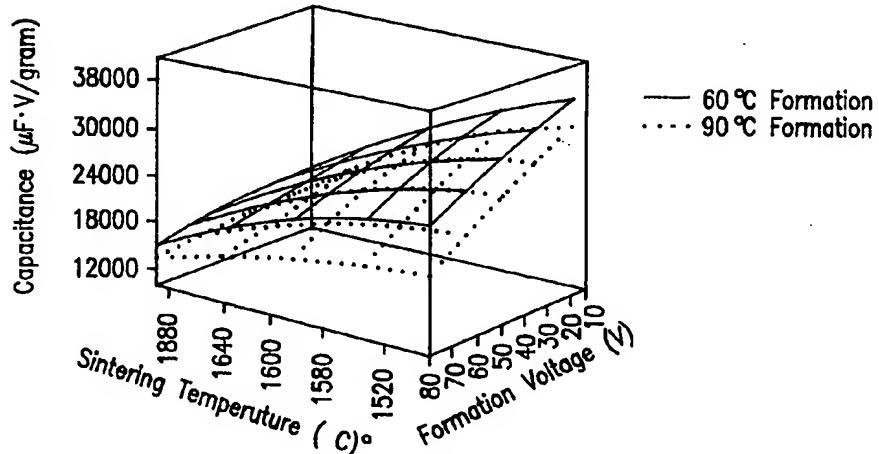


FIG. 3

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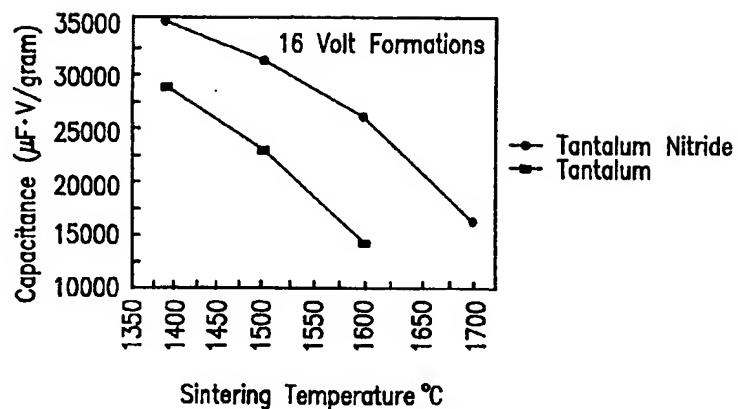


FIG. 4

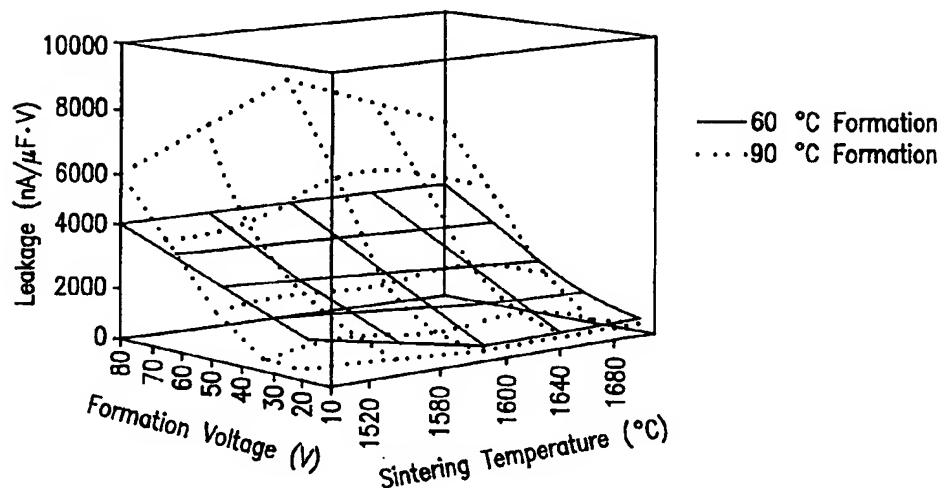


FIG. 5

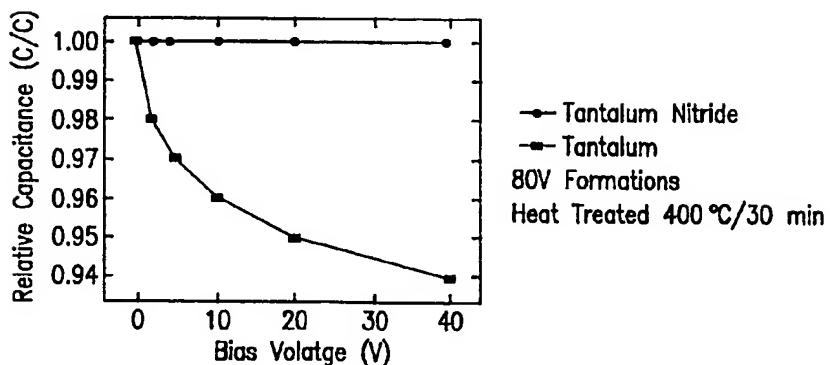


FIG. 6

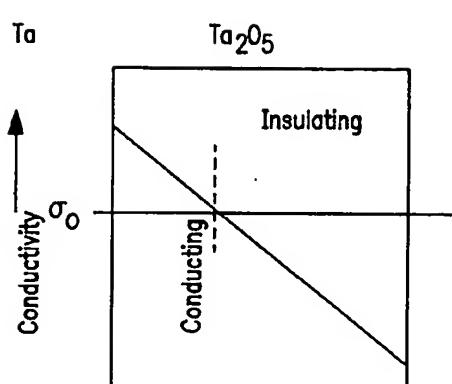


FIG. 7

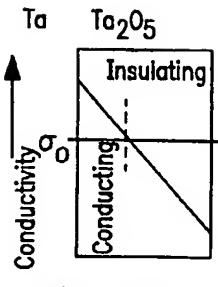


FIG. 8A

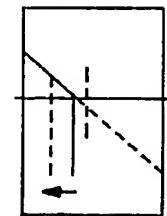


FIG. 8B

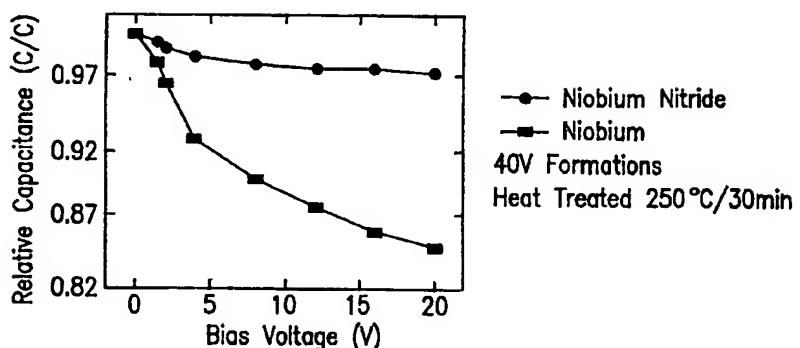


FIG. 9

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/03256

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :H01G 9/15, 9/145
US CL :361/305, 523

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 361/305, 523, 524, 525, 526, 528, 529, 530, 531, 532, 533, 534, 535, 540, 541; 29/25.03

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EAST

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 10-242004 (Naito) 11 September 1998 / (11.09.98), col. 1 lines 30-40, col. 3 lines 10-30, abstract.	1-3, 5
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Y		4
Y	US 5,754,394 (Evans et al.) 19 May 1998 / (19.05.98), abstract, claim 1	4
A	US 3,825,802 (Kumagai et al) 23 July 1974 / (23.07.74)	1-51
A	US 5,448,447 (Chang) 05 September 1995 / (05.09.95), abstract, col. 3 lines 60-68, col. 4 lines 60-65, col. 6 lines 42-46,	1-5
A	US 5,825,611 (Pozdeev) 20 October 1998 (20.10.98), abstract, col. 3 lines 49-55, col. 4 lines 15-51	1-5

Further documents are listed in the continuation of Box C. See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report 25 MAY 2000
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